

Nuclear Magnetic Resonance Hydrogen-Fluorine Spin-Spin Coupling

Purpose: Earth-field nuclear magnetic resonance (NMR) will be used to learn about pulsed NMR. Spin-lattice and spin-spin relaxation times of protons in water will be measured. The hydrogen-fluorine nuclear spin coupling constant in liquid trifluoroethanol will also be measured.



Introduction

Nuclear magnetic resonance is a field of complicated theory and many applications. Professor Paul Callaghan wrote the following in his introductory remarks¹ about NMR:

The scope of magnetic resonance is daunting, partly because the interactions of atomic nuclei with their atomic and molecular surroundings are subtle and diverse, and partly because the ways in which the nuclei can be made to respond to those terms by virtue of externally applied electromagnetic fields is almost boundless. The designer of magnetic resonance pulse sequences has at his or her disposal the depth of complexity possible when a composer writes a score for an orchestra.

This experiment uses a simple low-field instrument to study two fundamental aspects of NMR: spin relaxation and spin-spin coupling.

Theory

Many atomic nuclei have intrinsic spin. Hydrogen and fluorine, specifically the isotopes ^1H and ^{19}F , have nuclear spins of $\frac{1}{2}$. This experiment observes transitions of nuclear spins of hydrogen and fluorine under the influence of a magnetic field.

The spin quantum number is I , the quantum number for the z component of spin is m , and spin states are α and β .

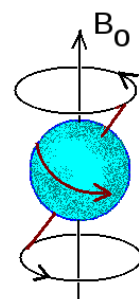
$$\begin{aligned} m = +\frac{1}{2}: \quad \hat{I}_z \alpha &= m \hbar \alpha = \frac{\hbar}{2} \alpha ; & \hat{I}^2 \alpha &= I(I+1) \hbar^2 \alpha = \frac{3}{4} \hbar^2 \alpha \\ m = -\frac{1}{2}: \quad \hat{I}_z \beta &= m \hbar \beta = -\frac{\hbar}{2} \beta ; & \hat{I}^2 \beta &= I(I+1) \hbar^2 \beta = \frac{3}{4} \hbar^2 \beta \end{aligned} \quad (1)$$

Nuclear-spin energy levels in an external magnetic field B_0 are simply $E_m = -m \gamma \hbar B_0$, where γ is the magnetogyric ratio. For ^1H , $\gamma = 2.675 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$. [Engel and Reid,² Table 28.1] For ^{19}F , $\gamma = 2.517 \times 10^8 \text{ T}^{-1} \text{ s}^{-1}$ [Halse, Magritek³] Considering that $m = \pm \frac{1}{2}$, energies are simply $\pm \frac{1}{2} \hbar \gamma B_0$, up-spin α is lower in energy than down-spin β . The energy difference is $\Delta E = E_{-1/2} - E_{1/2} = \gamma \hbar B_0$. As usual in spectroscopy, $\Delta E = h \nu = \hbar \omega$; this ω is the "Larmor" frequency.

$$\omega = \gamma B_0 \quad (2)$$

Note: ω is radians per second; $\nu = \omega / (2\pi)$ is in Hertz = Hz = s^{-1} .

Nuclear spins act as though they are magnetic moments precessing around the magnetic field B_0 . Up-spins, α , are partially aligned with B_0 and precess in the positive direction, as per the right-hand rule. Down-spins, β , are partially anti-parallel to B_0 and precess in the opposite direction. The z direction is defined by the direction of B_0 .



When many spins add together, as do those of the hydrogen nuclei in a sample of water, the net magnetization is along B_0 . A collection of N spins at temperature T will, at equilibrium, have net magnetization M :

$$M = N \gamma \hbar \langle m \rangle \quad (3)$$

where $\langle m \rangle$, the average z-component spin quantum number, is given by statistical thermodynamics.

$$\langle m \rangle = \frac{\sum_{m=-1/2}^{m=+1/2} m e^{-m \gamma \hbar B_0 / (k_B T)}}{\sum_{m=-1/2}^{m=+1/2} e^{-m \gamma \hbar B_0 / (k_B T)}} \quad (4)$$

Magnetization is so weak (because both γ and B_0 are small) that M simplifies to the following:

$$M = \frac{N \gamma^2 \hbar^2 B_0}{2 k_B T} \quad (5)$$

For this experiment, it is worth noting that M is proportional to γ^2 , so proton spectra should be more intense than fluorine spectra, for the same number of nuclei. In fact, the intensity ratio is γ^3 rather than just γ^2 because detection relies on voltage induced in the B_1 coil, and that voltage (called V_{out} below) is proportional to γ .

When taking a spectrum, the sample's spin magnetic moment M (which is the net sum of all the precessing nuclear magnetic moments) is first enhanced with a "polarizing" field B_p created by the outer magnet. The B_p pulse also tips M from the z axis onto the y axis. Magnetization M is initially directed along the Earth's magnetic field, which defines the z direction. Polarization field is along the x axis, which is the longitudinal axis of the instrument. Recall that, by the right-hand rule, z crossed into x generates torque in the y direction. The polarizing pulse is long enough and strong enough that it both increases the amplitude of M and reorients M to y .

After the polarizing pulse, M begins to relax in two ways: M_z returns slowly to its equilibrium value along the z axis, and (M_x, M_y) begin to "dephase". Dephasing refers to the individual nuclear magnetic moments, which were

temporarily aligned along M , spreading out. The time constant for that spread is T_2 . The time constant for re-growth of M_z , the relaxation known as spin-lattice relaxation, is T_1 . Often, T_1 is greater than T_2 . Component M_z is not detected by our instrument, so T_1 is not directly observed. The component of M in the (x,y) plane is detected by the B_1 coil. The sketches in

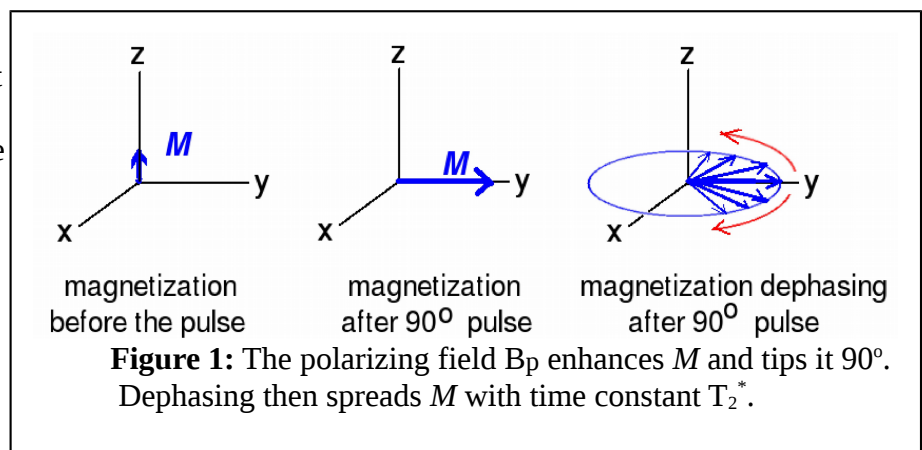


Figure 1 are like those shown by Engel and Reid in their Section 28.13.²

The effective, or observed, spin-spin relaxation time is T_2^* . It is related to the true spin-lattice time T_2 and field inhomogeneity, ΔB_0 . Inhomogeneity shortens T_2^* . Great inhomogeneity may make T_2^* so short that no signal at all is observed. Shimming fields along the x, y and z directions are added to reduce ΔB_0 , and so increase T_2^* . With our instrument located in room 301 of the Chemistry building, effective spin-spin relaxation times may be as long as a few seconds.

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \gamma \Delta B_0 \quad (6)$$

The polarizing pulse aligned the spins. As the spins dephase, their net magnetization is still precessing around the Earth's field (i.e., around the z axis), so the signal detected in the B_1 magnet both oscillates (with the Larmor frequency) and decays (with time constant T_2^*). That signal is called the free induction decay, or "FID". Figure 2 shows the FID and resulting spectrum from water, recorded on our EFNMR instrument.

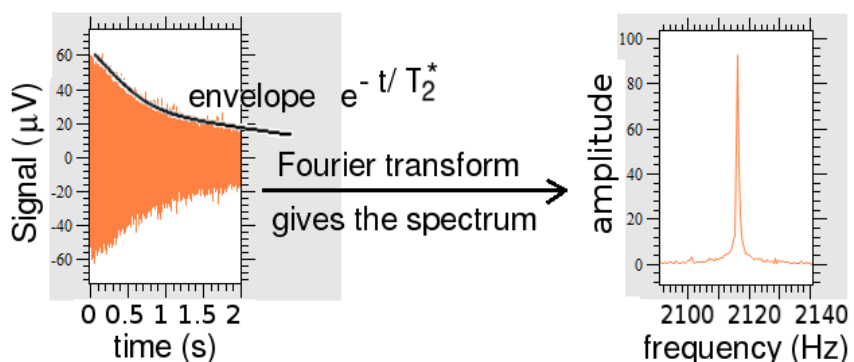


Figure 2. Free-induction decay from a water sample, and the spectrum.

Dephasing need not be the end of the experiment; it can be reversed. The "spin echo" technique (see section 28.13 of reference 2) uses a 180° (or " π ") pulse to flip magnetic moments across the x axis, converting dephasing to "re-phasing." Coherence is regained as the magnetic moments refocus, which leads to another peak (the "echo") in the FID. Figure 3 shows echoes caused by echo pulses at 0.2 and 0.6 s. (Figure 3 is a simulation, not real data.) Successive echo amplitudes (peaks at 0.4, and 0.8 s in Figure 3) decrease according to the spin-spin relaxation time T_2 , as

$$\text{echo amplitude} \propto e^{-t/T_2}. \quad (7)$$

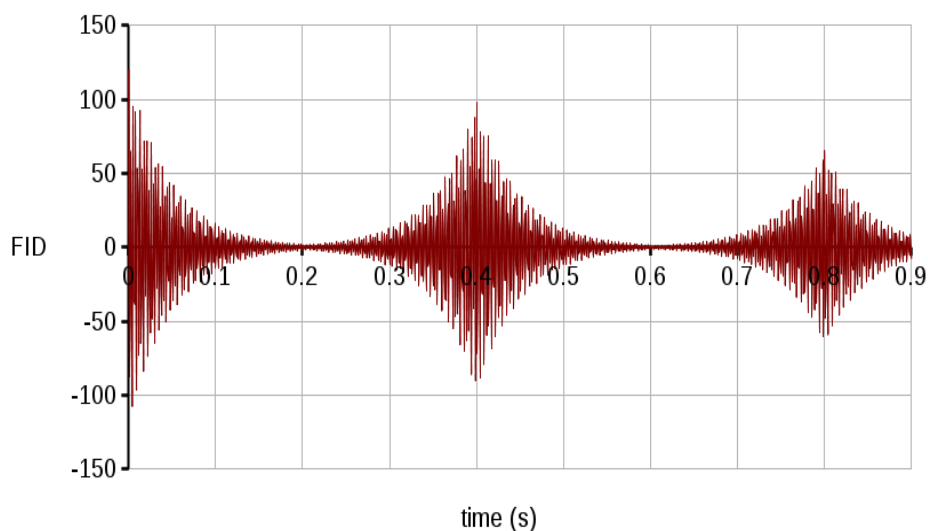


Figure 3. spin echoes

Successive echoes weaken because only the "inhomogeneous" dephasing due to field inhomogeneity and chemical shift is recovered by spin reversal; true "homogeneous" spin-spin relaxation is not.

The spin-lattice (or "longitudinal") relaxation time, T_1 , can be measured by varying the time between the polarizing pulse B_p and a subsequent 90° pulse. In the context of NMR, "lattice" simply means the surroundings with which spins can exchange energy. Suppose the magnetization along the z direction is M_z at time t , and that its equilibrium value is M_E , where the subscript "E" refers to the Earth's magnetic field. As spins exchange energy with their surroundings, M_z changes like so:

$$\frac{dM_z}{dt} = \frac{M_E - M_z}{T_1} \quad (8)$$

A solution to equation 8 is

$$M_z(t) = M_z(0)e^{-t/T_1} + M_E(1 - e^{-t/T_1}) \quad (9)$$

Because the polarizing pulse has a magnetic field much greater than the Earth's field, $M_z(0) \gg M_E$, the second term on the right-hand side can be neglected. That is,

$$M_z(t) = M_z(0)e^{-t/T_1} \quad (10)$$

The magnetization at time t is proportional to the FID amplitude at time t after the polarizing pulse. One can simply apply a 90° pulse at time t , measure the initial amplitude. After repeating the experiment with several values of t , $\ln(M_z(t))$ can be graphed *versus* t ; the slope equals $-1/T_1$.

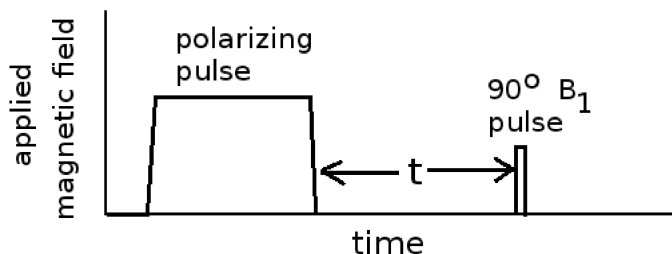


Figure 4. Pulse sequence for T_1 in the Earth's field.

In addition to measuring spin-spin and spin-lattice relaxation times, this experiment will record resonances of fluorine and hydrogen nuclei in 2,2,2-trifluoroethanol. The spin-spin coupling constant, J , of H and F nuclei will also be measured. (The constant may be called 3J or J^3 because the H and F nuclei are separated by three bonds.) Chemical shifts will not be observed. The OH proton and the CH_2 protons will appear at the same resonant frequency because chemical shifts of a few parts per million are too small to resolve in our low-field NMR. For example, a shift of 5 ppm from a resonant frequency of 2000 Hz is a shift of only 0.01 Hz. That is much smaller than our instrument's peak widths of approximately 1 Hz.

Proton and fluorine peaks will split into multiplets because of spin-spin coupling. The hydroxyl proton is not involved in this splitting because the OH proton exchanges rapidly between alcohol molecules and any traces of water present in the sample. The multiplets, then arise from three F nuclei interacting with two H nuclei; a 1:2:1 triplet and a 1:3:3:1 quartet. The following simple analysis relies on H and F resonances being well separated, with the H-F interaction then added on. In frequency units (Hz, units of ν or $\omega/2\pi$) the frequency shift due to H-F interaction is $\Delta\nu$.

$$\Delta\nu = m_H m_F J \quad (11)$$

The additivity condition (that interactions are "first order") is easy to check after spectra have been recorded.

$$J \ll \frac{|\omega_H - \omega_F|}{2\pi} \quad (12)$$

Figure 5 shows first the energy levels (but in frequency units, $\nu = E/h$) of an F nucleus and a pair of H nuclei, then the energy levels of FH_2 nuclei, but without interaction (i.e., with $J=0$). The third set of energy levels adds energy shifts due to interaction, as given in equation 6. Because the two H nuclei are treated as a pair, their m_H quantum numbers are -1, 0 and +1, corresponding to H nuclear spin configurations $\alpha\alpha$, $\alpha\beta$, $\beta\alpha$, and $\beta\beta$, respectively.

A similar analysis predicts that the CH_2 proton resonance splits into a 1:3:3:1 quartet, with frequency spacing J . The remaining proton, the hydroxyl proton, will still be at the unshifted proton resonance, so the protons will appear as a quartet (1:3:3:1) centered on a singlet of relative intensity 4 (i.e., a 1:3:4:3:1 intensity pattern). Engel and Reid discuss AX_2 and AX_3 cases in section 28.8.²

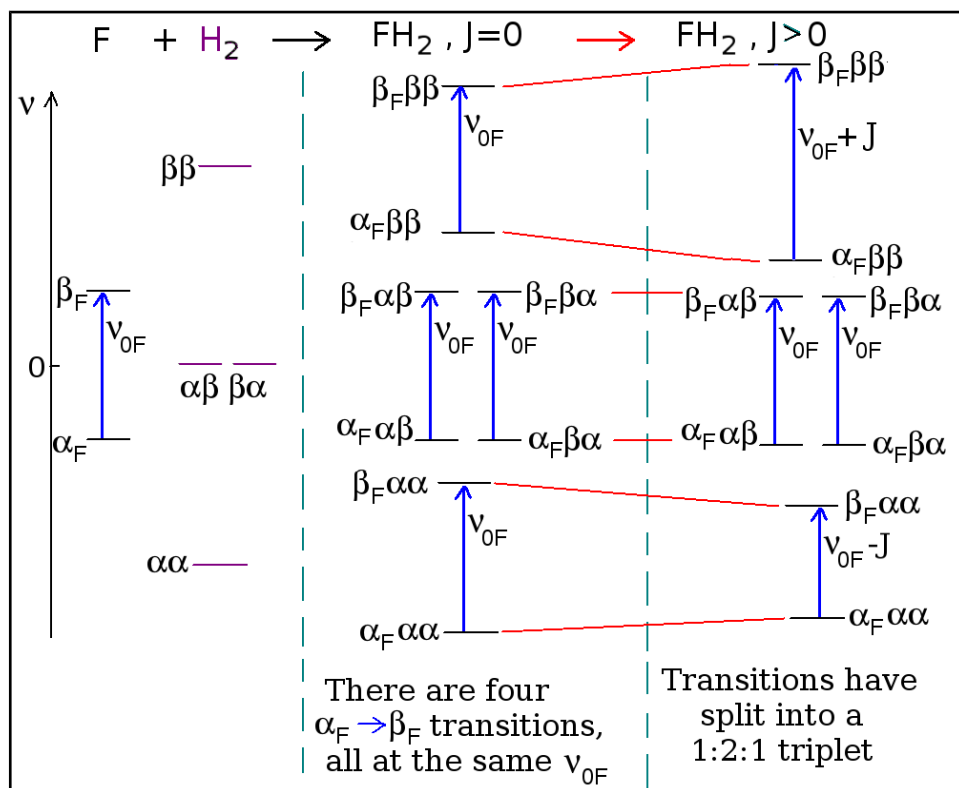


Figure 5. FH_2 energy levels and transitions.

Within the same first-order approximation used to predict splitting patterns, peak intensities are simply proportional to the number of nuclei and to γ^3 . If a spectrum is not too noisy, the integrated area under a peak is a good measure of its intensity. Trifluoroethanol contains the same number of fluorine and hydrogen nuclei but fluorine has a smaller γ , so the integral of fluorine peaks should be smaller than the integral of hydrogen peaks.

The Earth's Field NMR (EFNMR) Instrument

The instrument contains three coaxial tubes wrapped with wire, the coils. The three coaxial tubes are pictured at right.³ The large outer coil is the "polarizing coil," used to align sample spins. The innermost coil, the B_1 coil, measures and excites precessing net magnetization. The middle tube contains four coils: gradient coils to adjust ("shim") the magnetic field in the x , y and z directions, and a second x coil that is used for pulsed-gradient NMR. The electronics box, the "spectrometer," communicates with the *Prospa* software that is on a computer, sends power to the coils as needed, and collects response from the B_1 coil.

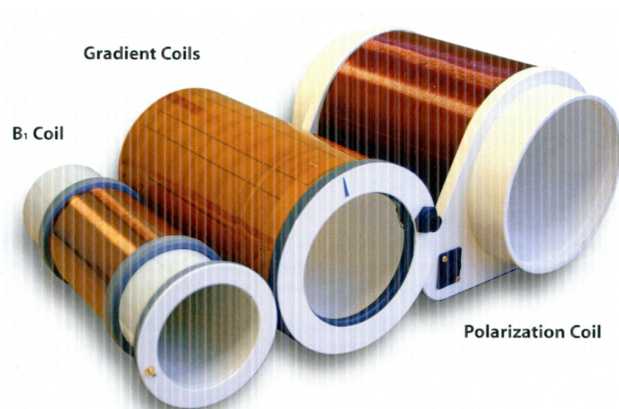


Figure 6. Magritek EFNMR coils (ref. 3)

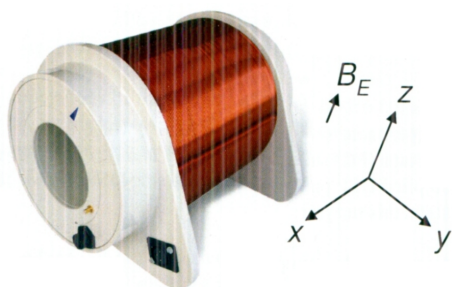


Figure 7. EFNMR probe and axis conventions. (ref. 3)

As shown in Figure 7, at left, the x axis lies along the axes of the tubes. The y and z axes are perpendicular to the probe's axis, with z being along the Earth's magnetic field, B_E .

Reagents

500 mL of deionized water	in the lab on tap
500 mL of 2,2,2-trifluoroethanol	in the lab

Procedure

setup and shim the EFNMR instrument

The EFNMR may already be in place; check to be sure. The EFNMR on its plastic cart should be between benches, with the coil axis perpendicular to magnetic N-S. (There is a conventional compass for locating North.) The arrow on the end of the instrument should point along the magnetic field (there is a three-axis compass for the purpose), likely a little off vertical.

Turn on the spectrometer. Start the *Prospa* software on the computer. Connect the usb cable from the spectrometer to the computer. Prepare to use a flash drive to save data and images from the experiment.

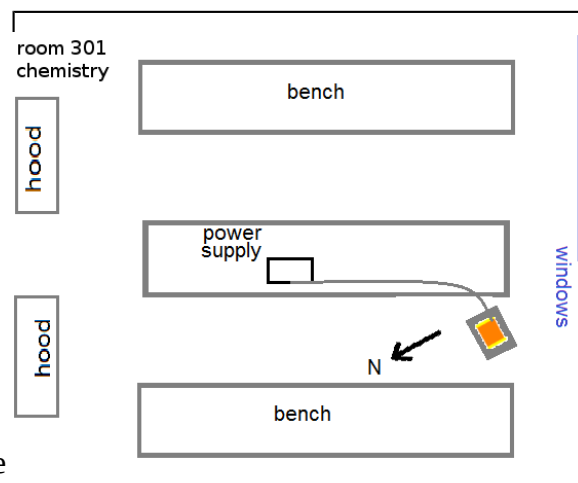


Figure 8. placement of the EFNMR

With no sample in the instrument (i.e., the cavity empty) select the *MonitorNoise* experiment from *Prospa*'s EFNMR menu. Set the "output location" to a working directory on your flash drive. Let *MonitorNoise* run for a few seconds. The RMS noise should be below 10 μV . In the 1-D graph sub-window, the "Edit" menu has an entry to allow copying one or all (two) graphs, for eventual inclusion in a report.

Fill the 500-mL plastic bottle with water (either tap or distilled) and place it in the EFNMR probe cavity. Open the *PulseAndCollect* experiment on the EFNMR menu. This experiment runs the polarizing pulse, then the B_1 90° pulse, then collects the FID, and finally Fourier-transforms the FID into a spectrum. The spectrum should be similar to the sample in Figure 9, but likely shorter and broader. Note the frequency at which the maximum occurs. If the B_1 frequency is not already set to that value, set it. Save the spectrum for your report.

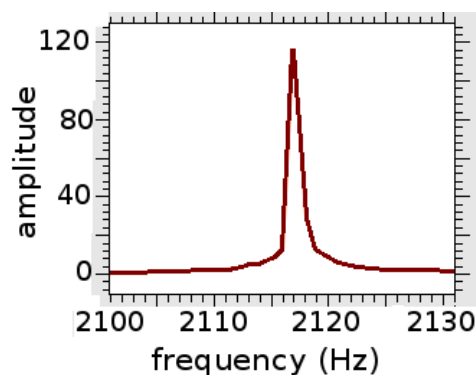


Figure 9. sample spectrum of water

The building and its contents alter the Earth's magnetic field, resulting in a local field that is weaker and inhomogeneous. Shims (linearly varying fields in the x , y and z directions) are added to compensate for inhomogeneity. Good shims produce a long-lived FID and a narrow peak in the spectrum. Run the *AutoShim* experiment from the EFNMR menu. This will take approximately 15 minutes, maybe less if the instrument has not been moved since the last time it was shimmed. The auto-shimming program attempts to increase the amplitude of water's proton resonance peak.

When the *AutoShim* experiment is done, note the frequency of the peak. It will be approximately the same as the B_1 value observed above. If it is not exactly the same, change B_1 in the *AutoShim* dialog

box. If B_1 changed by much (more than 6 Hz, say) rerun *AutoShim*.

Save all three graphs (FID, spectrum, and amplitude-iteration history) for your report. Notice that in addition to creating graphs, *Prospa* writes to a text window, the "CLI" (command-line interface) window. It will sometimes be convenient to read or copy text data from the CLI window. Copy the final shim values from the CLI window to a file for your report.

A B_1 magnetic pulse can be applied to rotate the sample's magnetic moment 90° or 180° . The pulse length required for each of those rotations should be optimized. Approximate values are 1.5 ms for 90° , 2.7 ms for 180° . An optimal 90° pulse gives maximum signal, a 180° pulse should give zero signal. Open the *B1Duration* experiment under the EFNMR menu. Set the minimum B_1 to 0.5 ms. Set the number of steps to 15. Choose a B_1 step size that makes the maximum B_1 about 3.5 ms. Run the experiment. Read and note the 90° pulse length at the maximum and the 180° pulse length at the following minimum. Save the graph for your report.

spin-lattice relaxation time T_1

Continue using the water sample in the 500-mL bottle. Because T_1 depends on temperature, and comparison to literature values will be good, use a thermometer to measure the water's temperature. Record the temperature for future reference.

On *Prospa*'s EFNMR menu, open the *T1Be* experiment. The "Be" part of the name refers to measuring T_1 in the Earth's magnetic field. The *T1Be* experiment repeats a basic pulse-and-collect experiment multiple times (specified by "number of steps") and graphs the amplitude *versus* the time delay (" t " in equation 10). Set the minimum t ("Pre-90 minimum delay time" in the dialog box) and choose a step size and number of steps to scan t out to 5 or 6 seconds in 10-20 steps. Run the experiment. *Prospa* will calculate T_1 as the experiment runs, by fitting the data to equation 10. Save the graph, the data (from the CLI window), and T_1 .

spin-spin relaxation time T_2

Open the *T2* experiment from the EFNMR menu. This experiment takes a spin-echo spectrum multiple times, varying the echo time τ_E . The time t to the center of the echo is $t=2\tau_E$. Exponential decay of amplitude, A , will be fit by *Prospa* equation 13 as the experiment proceeds.

$$\frac{A(\tau_E)}{A_0} = e^{-2\tau_E/T_2} \quad (13)$$

In the *T2* dialog box, set a B_1 frequency range ("display range") that includes the peak. The peak will be integrated over the integration interval that is set in the dialog box. The spin-echo time will be varied from the "Minimum echo time" (200-400 ms, say) in steps of "Echo time step". Choose the number of steps and the time step so that the maximum echo time is approximately T_1 or longer. Set the 90° and 180° pulse times to the values you found earlier.

For this experiment, the instrument must be temporarily de-shimmed. That is, the shim values must be changed from their optimal values. De-shimming is done to reduce T_2^* so that the FID decays to zero before the echo pulse is applied, at even the minimum echo time. To de-shim temporarily, just for the T_2 experiment,

- (i) Click the "Shims" button.
- (ii) Use the sliders to change the shim values. (It seems that *typing* new shim values has a different effect.)
- (iii) Click "Close."
- (iv) When asked about replacing the saved shims, click "No."
- (v) When one wants to return to using the optimized shims, click "Shims" again, then "Reset," and "Close." That will be good to do after determining T_2 .

De-shim a little. In this case, "a little" means enough so that T_2^* falls below the minimum echo time, but not so much that the peak amplitude falls below the RMS noise. That is, the peak should become broad and weak but should not disappear.

Run the T_2 experiment. At the first echo time, you should see that the FID decays nearly to zero by the time of the echo pulse, but the spectrum still shows a peak. If not, de-shim more (faster FID decay) or less (greater peak amplitude). If the spectrum collapses into the noise at long τ_E , re-do the run with fewer or shorter τ_E steps.

Save the graph for your report. Note the value of T_2 . Copy the graphs from the 1-D graph window and the data (the spin-echo amplitudes) from the CLI window for your report.

For the Discussion section of your report, find literature values of T_1 and T_2 for protons in liquid water. For example, T_1 values were reported by Simpson and Carr in 1958.⁵ Baub and Duns⁶ gave values of both T_1 and T_2 .

hydrogen-fluorine spin-spin coupling in trifluoroethanol

preliminary calculations

In order to record a spectrum of fluorine nuclei, the relationship $\omega = \gamma B_0$ can easily be used to calculate the frequency at which F should resonant.

$$\omega_F = \frac{\gamma_F}{\gamma_H} \omega_H = \frac{2.517}{2.675} \omega_H = 0.941 \omega_H. \quad (14)$$

If, for example, $\omega_H = 2109$ Hz, then $\omega_F = 1985$ Hz. Because the fluorine frequency is close to the proton frequency, for a low-field NMR, we could record the fluorine spectrum using the same instrument settings we used for hydrogen. However, better fluorine spectra can be obtained by re-tuning. Tuning means changing the software-controlled capacitance of the B_1 coil. The capacitance, C , of the coil is related to its resonant frequency as $\omega \propto 1/\sqrt{C}$. So, to change the resonant frequency to that of fluorine, we could change C as follows:

$$C_F = C_H \frac{\omega_H^2}{\omega_F^2} = C_H \left(\frac{\gamma_H}{\gamma_F} \right)^2 = 1.063^2 C_H = 1.129 C_H.$$

Because we want to see *both* F and H nuclei in the *same* spectrum, it is better to choose a capacitance mid-way between the resonant capacitances for H and for F.

$$C_{\text{midway}} = \frac{C_H + C_F}{2} = C_H \frac{1 + \left(\frac{\gamma_H}{\gamma_F}\right)^2}{2} = C_H \frac{1 + 1.129}{2} = 1.065 C_H \quad (15)$$

Likewise, the frequency midway between fluorine and proton resonances should be

$$\omega_{\text{midway}} = \frac{\omega_H + \omega_F}{2} = \omega_H \frac{1 + \left(\frac{\gamma_F}{\gamma_H}\right)}{2} = \omega_H \frac{1 + 0.941}{2} = 0.970 \omega_H \quad (16)$$

procedure

Open the *PulseAndCollect* experiment on the EFNMR menu. Note the frequency and coil capacitance shown in the dialog box. They should be ω_H and C_H . Using equations 14, 15 and 16, calculate the resonant frequency of fluorine, ω_F , and the "midway" capacitance and frequency. In the *PulseAndCollect* dialog box, set the capacitance and the B_1 frequency to the midway values. Type in a "Display range" large enough to encompass both fluorine and hydrogen peaks.

Put a bottle of 2,2,2-trifluoroethanol into the probe cavity. Record the spectrum. The spectrum should contain a lower-frequency triplet for fluorine and a higher-frequency group of five peaks for hydrogen, as discussed in the Theory section and sketched below in Figure 10.

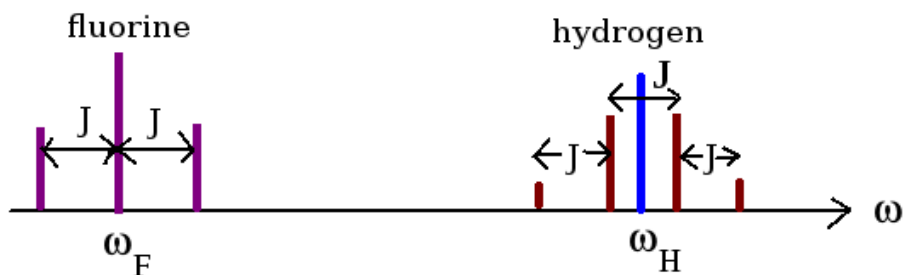


Figure 10. Schematic spectrum of trifluoroethanol.

If the midway frequency you calculated and entered is not roughly in the middle between fluorine and hydrogen peaks, adjust it. Choose some number of scans greater than one, click the "average" option, and record the NMR spectrum of trifluoroethanol.

Integrate the peaks. To integrate:

◇ Under the 1D menu, chose *integrate1d*.

◇ Choose the "Select Region" cursor tool to draw a box around peaks, that range is immediately transferred to the "integrate 1d region" dialog.



In your report, compare the ratio of peak integrals to that expected based on the number of H and F atoms in the sample, correcting for the intrinsically lower signal expected from fluorine: the factor γ^3 enters, as mentioned in the Theory section.

From your spectrum, calculate J. The weak outer CH_2 peaks may not be resolved, but J can still be read

between the inner two CH₂ peaks. Find a literature value for comparison. Here are some possible sources: A literature value of the hydrogen-fluorine coupling constant in trifluoroethanol is given by Trabesinger, *et al.*, in reference 7 (there called "J³"). Another literature value is given by Bernarding, *et al.*, in reference 8 (there called "J³"). Yet another value is given by Zhang, *et al.* in reference 9 (there called the "proton-fluorine coupling strength").

Use your spectral results to check how well the first-order condition given in equation 12 applies.

Before closing the *PulseAndCollect* experiment, it would be well to reset the capacitance and frequency to their proton values.

References

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